

# Symmetry consideration and $e_g$ bands in NdNiO<sub>3</sub> and YNiO<sub>3</sub>

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## Abstract

Group theoretical analyses are applied to the magnetic and electronic structures of NdNiO<sub>3</sub> and YNiO<sub>3</sub>, whose electronic structures have been studied very recently by the LSDA+U method. The space groups of the crystallographic structure of these materials are  $Pbnm$  and  $P2_1/n$ , respectively.[1,2] There are no Jahn-Teller distortion modes consistent with observed propagation vector of spin polarized neutron-diffraction. Two possible spin configurations (magnetic space groups)  $C_a mc2_1$  and  $P_b a$  are derived from  $Pbnm$  for NdNiO<sub>3</sub>. Then the electronic structures with each symmetry are studied by using the tight-binding model. Clear separation of partial density of states exists in  $P_b a$  but does not in orthorhombic  $C_a mc2_1$ . The combination of results of the present work and the previous LSDA+U calculation shows that the ground state magnetic structure of NdNiO<sub>3</sub> is monoclinic  $P_b a$ . NdNiO<sub>3</sub> has only one kind of Ni sites, while YNiO<sub>3</sub> has two inequivalent Ni sites. The magnetic structure of YNiO<sub>3</sub> is monoclinic  $P_b 2_1/a$ , if one assumes no magnetic moment on Ni ions (Ni<sup>4+</sup>) on one of these inequivalent sites.

*Key words:* A.magnetic materials, A.oxides, D.electronic structure, D.magnetic structure

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The perovskite nickelates NdNiO<sub>3</sub> and YNiO<sub>3</sub> are anti-ferromagnetic insulators in their low temperature phases. Their magnetic structures are characterized by a propagation vector  $\vec{k} = (\frac{1}{2}, 0, \frac{1}{2})$  [3] and, therefore, the magnetic unit cell is a  $2 \times 1 \times 2$  supercell of the original crystallographic unit cell. The spin alignment in these two nickelates is quite unique one such that the symmetrical coexistence of ferro- and antiferromagnetic couplings along the three pseudo cubic axes as  $\cdots \text{Ni}^\uparrow - \overset{\text{FM}}{\text{O}} - \text{Ni}^\uparrow - \overset{\text{AFM}}{\text{O}} - \text{Ni}^\downarrow - \overset{\text{FM}}{\text{O}} - \text{Ni}^\downarrow \cdots$ . In YNiO<sub>3</sub>, the charge disproportionation  $2\text{Ni}^{3+} \rightarrow \text{Ni}^{2+} + \text{Ni}^{4+}$  and the symmetrical coexistence of ferro- and antiferromagnetic couplings are both observed, though the Ni<sup>4+</sup> ions have small magnetic moments. [2] Diffraction experiments in NdNiO<sub>3</sub> do not show accompanied Jahn-Teller distortion associated with the orbital polarizations of Ni  $e_g$  orbitals.

Very recently, we have calculated the electronic structures of the perovskite nickelates  $\text{NdNiO}_3$  and  $\text{YNiO}_3$  by the LSDA+U method which will be published elsewhere. [4] We observed in that study no orbital ordering in  $\text{NdNiO}_3$  and the charge disproportionation in  $\text{YNiO}_3$ . The basic consideration by the group theory about the magnetic structures, the possibility of the Jahn-Teller modes and the simple picture of the  $e_g$  bands in these structure are given in the present report.

*Crystallographic space group:* The crystallographic space groups of  $\text{NdNiO}_3$  and  $\text{YNiO}_3$  are orthorhombic  $Pbnm$  and monoclinic  $P2_1/n$ , respectively.  $P2_1/n$  is the subgroup of  $Pbnm$  and their group elements are as follows;  $Pbnm = P2_1/n \otimes \{E, \{\sigma_x|\frac{1}{2}\frac{1}{2}0\}\}$ ,  $P2_1/n = \{E, \{\sigma_y|\frac{1}{2}\frac{1}{2}\frac{1}{2}\}, I, \{C_{2y}|\frac{1}{2}\frac{1}{2}\frac{1}{2}\}\}$ . where  $E$  is the identity operator,  $I$  the inversion operator,  $\sigma_x$  the mirror operation with respect to the  $y$ - $z$  plane and  $C_{2y}$  the two-fold rotation operator with respect to the  $y$  axis. Both  $\text{NdNiO}_3$  and  $\text{YNiO}_3$  systems contain four Ni ions in their crystallographic unit cells and each locates on the inversion center. Four Ni sites are labeled as  $\text{Ni}(1)=(\frac{1}{2}, 0, 0)$ ,  $\text{Ni}(2)=(0, \frac{1}{2}, 0)$ ,  $\text{Ni}(3)=(\frac{1}{2}, 0, \frac{1}{2})$  and  $\text{Ni}(4)=(0, \frac{1}{2}, \frac{1}{2})$ . In  $\text{NdNiO}_3$ , all four nickel positions are equivalent. In  $\text{YNiO}_3$ , no symmetry operations transfer a position  $\text{Ni}(1)$  or  $\text{Ni}(4)$  to that of  $\text{Ni}(2)$  or  $\text{Ni}(3)$ . Therefore, there are two inequivalent positions of Ni ions in  $\text{YNiO}_3$ .

*Magnetic space group:* First we consider the magnetic space groups generated from the crystalline space group  $Pbnm$  with the experimentally observed propagation vector  $\vec{k} = (\frac{1}{2}, 0, \frac{1}{2})$ . The translation vector along the  $\alpha$ -axis of crystallographic  $Pbnm$  structure is denoted by  $\vec{T}_\alpha$ . The system is the orthorhombic base centered lattice and the (orthogonal) primitive translation vectors should be  $\{2\vec{T}_x, \vec{T}_y, 2\vec{T}_z\}$ . The nonorthogonal translation vectors  $\vec{T}_x + \vec{T}_z$  and  $\vec{T}_x - \vec{T}_z$  transform lattice points at corners of the Bravais lattice to those at the base centers.

Assuming the orthorhombic magnetic unit cell, one of possible spin arrangements is the structure where  $\text{Ni}(1)$ ,  $\text{Ni}(2)$ ,  $\text{Ni}(3)$ ,  $\text{Ni}(4)$  in a unit cell of  $Pbnm$  have the same spins and the translation operators  $\vec{T}_x$  or  $\vec{T}_z$  flips the spins of Ni ions. [3] Then the ferromagnetically aligned spins are confined within a one-dimensional rod extending towards  $y$ -direction. The doubled translation vectors along the  $x$ - and  $z$ -axes prohibit the screw operator  $2_1$  along the  $x$ - and  $z$ -axes. [5] Then the unitary part of the resultant magnetic space group should be  $Pmc2_1 = \{E, \{C_{2y}|\frac{1}{2}\frac{1}{2}\frac{1}{2}\}, \{\sigma_x|\frac{1}{2}\frac{1}{2}0\}, \{\sigma_z|00\frac{1}{2}\}\}$ . An augmenting operator with the time-reversal operator is the translation one  $\vec{T}_x$  and the magnetic translation vector should be  $2\vec{T}_x$ . The resultant magnetic space group is base centered orthorhombic  $C_a mc2_1$ .

Another possible spin arrangement associated with  $Pbnm$  and  $\vec{k} = (\frac{1}{2}, 0, \frac{1}{2})$  is that where the same spins are located on Ni ions in a parallelepipedon

spanned by translation operators  $\{\vec{T}_x, \vec{T}_y, \vec{T}_z - \vec{T}_x\}$ . In this structure, the two-fold rotational operator with respect to the  $z$ -axis and the mirror operator with respect to the  $x$ - $y$  plane are prohibited because these contradict to the monoclinic Bravais lattice. The screw operator  $2_1$  along  $x$ -axis is also prohibited due to cell doubling. There remain only two symmetry operators  $E$  and  $\{\sigma_y|\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  the glide operator along the monoclinic axis  $\vec{T}_z - \vec{T}_x$ . Because the augmenting operator with the time-reversal operator is the translation  $\vec{T}_x$ , the resultant magnetic space group is monoclinic  $P_ba$ . The magnetic structure of  $\text{NdNiO}_3$  with  $P_ba$  symmetry is of double layers of the (101) plane, on which all Ni ions have the same spins.

In  $\text{YNiO}_3$ , there are two inequivalent Ni sites, as already stated. If there exists no magnetic moment on Ni sites, e.g. Ni(2) and Ni(3), the system has the inversion symmetry around the sites of Ni(1) and Ni(4), and the magnetic space group should be  $P_b2_1/a$ . This is actually the case for  $\text{YNiO}_3$  where the charge disproportionation  $2\text{Ni}^{3+} \rightarrow \text{Ni}^{2+} + \text{Ni}^{4+}$  occurs and the magnetic moment of  $\text{Ni}^{4+}$  is zero.

*Jahn-Teller distortion:* In many transition metal perovskites, the Jahn-Teller distortion coexists with the complicated spin and orbital orderings. In perovskite nickelates, no Jahn-Teller distortion has been reported yet. A possibility of the Jahn-Teller mode consistent with the space group  $Pbnm$  and the propagation vector  $\vec{k} = (\frac{1}{2}, 0, \frac{1}{2})$  can be discarded in a following way. A unit cell of  $Pbnm$  contains four  $\text{NiO}_6$  octahedra which share O ions with each other. Let us consider the  $E_g$  Jahn-Teller modes in two octahedra  $\text{Ni}(1)\text{O}_6$  and  $\text{Ni}(4)\text{O}_6$  which do share no O ions. There are two two-dimensional irreducible representations in the  $\vec{k}$ -group  $G(\vec{k} = (\frac{1}{2}, 0, \frac{1}{2}))$ , and they are listed in Ref. [3]. The only elements of non-zero character are  $E$  and  $\{\sigma_y|\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  and  $\chi(\{\sigma_y|\frac{1}{2}\frac{1}{2}\frac{1}{2}\}) = \pm 2$ . Therefore, the projection operator on those representations are  $P = d/g \sum_{R \in G} \chi(R)^* R = \frac{1}{2}(\{E|000\} \pm \{\sigma_y|\frac{1}{2}\frac{1}{2}\frac{1}{2}\})$ . When  $\{\sigma_y|\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$  operates on  $Q^1u$ , resultant mode equals to  $Q^4u$  and vice versa. Here  $Q^j u$  is the  $E_g$   $u$  mode of  $\text{Ni}(j)\text{O}_6$  ( $j = 1, 4$ ). Then basis vectors of the lattice distortion that belong to these irreducible representations are  $Q^1u \pm Q^4u$  in two octahedra  $\text{Ni}(1)\text{O}_6$  and  $\text{Ni}(4)\text{O}_6$ . The propagation vector  $\vec{k} = (\frac{1}{2}, 0, \frac{1}{2})$  requires that the translation operation of  $\vec{T}_x$  or  $\vec{T}_z$  changes the sign of a displacement vector. The resultant displacement vectors are shown in Fig. 1. Now the displacements of all O ions of  $\text{Ni}(3)\text{O}_6$  have been determined, because they are contained either in  $\text{Ni}(1)\text{O}_6$  or in  $\text{Ni}(4)\text{O}_6$ . The resultant distortion of the  $\text{Ni}(3)\text{O}_6$  octahedron is an ungerade mode, as seen in Fig. 1, and cannot be generated from  $E_g$  mode on this octahedron. The same arguments can be applied to other distortion modes. This is the proof that the  $E_g$  mode in one octahedron cannot be transferred to all octahedra over the whole unit cell.

*Structure of  $e_g$  bands:* Because the 3d  $e_g$  orbitals in Ni ions are partly filled, the highest occupied (HOMO) states should be  $e_g$  bands. Since the structures of

NdNiO<sub>3</sub> and YNiO<sub>3</sub> have been discussed group theoretically, the band structure of the  $e_g$  orbitals can be analyzed from the similar group theoretical view point and this analysis would be useful to understand the calculated electronic structure of these systems by the LSDA+U. [4] The discussion can be based on a tight-binding Hamiltonian of single spin component and one can neglect electron transfer from one spin site to sites with opposite spin. Since there are no Jahn-Teller modes and the tilting angle of the NiO<sub>6</sub> octahedra is small, distortion can be neglected and an ideal cubic structure is assumed. The Hamiltonians do not have any terms of the Slater-Koster parameter  $V_{dd\pi}$  due to this high symmetry.

First, let us discuss the case of  $C_{4v}$ . Electrons can transfer only within a one-dimensional rod and the ferromagnetic cell extending along the  $y$ -axis. The  $e_g$  orbitals are located at four vertices of a unit cube, i.e. (0, 0, 0), (0, 0, 1), (1, 0, 0), (1, 0, 1), with a translation vector  $\vec{t} = (1, 1, 0)$ . The parameter  $V_{dd\sigma}$  and  $V_{dd\delta}$  are chosen to equal to  $-1$  and  $-0.1$ , respectively, and the diagonal atomic energy to be zero. Figure 2 shows the resultant energy bands  $E(k)$  in comparison with those by the LSDA+U method. [4] Because this one-dimensional lattice is bipartite, the  $E(k)$  curves are symmetric with respect to  $E = 0$ . As occupation in Ni case is just one electron per each site, the Fermi energy is at the energy zero  $E_F = 0$ . The result of the tight-binding Hamiltonian can reproduce the essential feature of the  $e_g$  band. Two widely dispersive and two narrow bands are occupied and they have no dispersion along  $x$ - and  $z$ -axis. Two dispersive curves are crossing at the Fermi level. The  $\vec{k}$ -value of the crossing point actually depends on the ratio  $V_{dd\delta}/V_{dd\sigma}$ , because the two-fold degeneracy at the Fermi level is not due to the crystallographic symmetry. The separation of partial density of states can be seen very clearly in the partial density of states in the present tight binding model, as shown in Fig. 2c. The model Hamiltonian keeps much higher symmetry than the actual system and the actual system opens the gap as seen in Fig. 2a

Next, let us consider the case of  $P_6a$ . The (101) plane of the  $P6mm$  structure corresponds to the (111) plane of the cubic lattice. Hereafter, the subscript “ $c$ ” denotes the cubic lattice as (111) <sub>$c$</sub> . Centers of atomic  $e_g$  orbitals (Ni ions) locate at vertices of a unit cube; (0, 0, 0) and (0, 0, 1) with a translation vector  $\vec{a} = (1, 0, -1)$  and  $\vec{b} = (0, 1, -1)$ . Since the system has the three-fold rotational symmetry around [111] <sub>$c$</sub>  axis, the Brillouin zone is a hexagon. The unit cell contains two Ni atoms and, therefore, four bands exist in the Brillouin zone. Two of them have the dispersion proportional to the  $V_{dd\delta}$  and the other two have larger dispersion. They touch each other at the Fermi energy  $E_F$ . Each band is symmetric around  $E_F$ , because the lattice is bipartite. The contour plot of the band energy  $E(\vec{k})$  touching  $E_F$  is shown in Fig. 3, where the  $V_{dd\sigma}$  and  $V_{dd\delta}$  are set to be  $-1.0$  and  $-0.1$  respectively, together with the band structures of the LSDA+U calculation. [4] The Fermi surface is reduced to just points, six vertices of the first Brillouin zone (BZ), and there is two-fold degeneracy at the

Fermi surface due to three-fold rotational symmetry. Therefore, this system is a marginal metal. The eigen states at the vertex of the BZ are corresponding to bonding and anti-bonding states of  $\varphi_{u\pm}$  on each adjacent plane, where  $\varphi_{u+} = -\frac{1}{\sqrt{2}}(\varphi_{3z^2-r^2} + i\varphi_{x^2-y^2})$  and  $\varphi_{u-} = \frac{1}{\sqrt{2}}(\varphi_{3z^2-r^2} - i\varphi_{x^2-y^2})$ . This is not only the case at the Fermi energy. The system of the model Hamiltonian is the trigonal  $D_{3d}$  and the basis wavefunctions are also  $\varphi_{u\pm}$ , which are the basis of the  $E_g$  representation. Therefore, this system does not cause the orbital polarization at all, and the partial density of states by the tight-binding model is shown in Fig. 3c. Because this system is a marginal metal, the small perturbation easily lifts the two-fold degeneracy at the Fermi surface and leads the system to the insulating phase. Actually, the gap positions in Fig. 3a are identical to the vertices of the BZ in Fig. 3b and the system has no three-fold symmetry.

Both simple tight-binding models based on  $C_{4v}$  and  $P_6$  spin alignment, give metallic bands in contradiction to the fact that  $\text{NdNiO}_3$  is insulator, simply because the models have much higher symmetry than that of realistic models. The result of LDA+U calculation, which is referred before, shows that the bands in  $P_6$  open the gap of 0.11 eV without orbital polarization and those in  $C_{4v}$  also open the gap of 0.24 eV with a slight orbital order. [3] Since the orbital polarization has not been observed and no Jahn-Teller distortion reported, the spin alignment of  $P_6$  is probably the case.

The charge disproportionation  $2\text{Ni}^{3+} \rightarrow \text{Ni}^{2+} + \text{Ni}^{4+}$  is observed experimentally in  $\text{YNiO}_3$ . This is accompanied by the crystallographic symmetry reduction from  $Pbnm$  to  $P2_1/n$ . If the spin on  $\text{Ni}^{4+}$  ions is zero, then only one magnetic structure  $P_62_1/a$  is allowed. In this case, the charge polarization (charge order) opens the gap. Our LSDA+U calculation gives the band gap of 1.03 eV in  $\text{YNiO}_3$ . [4] Experimentally observed magnetic moment on  $\text{Ni}^{4+}$  ions is not zero and this discrepancy may be due to the dynamical effect of spins. [2]

*Conclusion:* We discussed very details of the magnetic space group for  $\text{NdNiO}_3$  and  $\text{YNiO}_3$ , and discarded the possibility of the Jahn-Teller distortion extending over the whole magnetic cell. The electronic structures of  $e_g$  bands are analyzed by the tight-binding Hamiltonian, and compared with the calculated results by the LSDA+U method. [4]

The present tight-binding model, in both cases of  $\text{NdNiO}_3$  and  $\text{YNiO}_3$ , is so simple and several symmetry elements are not included in the Hamiltonian. Then the resultant band structure is of the marginal metal but not of insulator. This discrepancy is not serious at all.

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Fig. 1. The displacement vectors corresponding to a basis function of group of  $\vec{k} = (\frac{1}{2}, 0, \frac{1}{2})$  of  $Pbnm$ . Center of each octahedron is occupied by Ni ion; Ni(1)=( $\frac{1}{2}, 0, 0$ ), Ni(2)=( $0, \frac{1}{2}, 0$ ), Ni(3)=( $\frac{1}{2}, 0, \frac{1}{2}$ ), Ni(4)=( $0, \frac{1}{2}, \frac{1}{2}$ ). The Ni ions with prime marks can be obtained from the original (without a prime) ions by the primitive translations.

Fig. 2. Energy bands  $E(\vec{k})$  for one spin component in NdNiO<sub>3</sub> with  $C_{4v}$  by the LSDA+U method (a) and those by the tight binding model (b). The Slater-Koster parameters  $V_{dd\sigma}$  and  $V_{dd\delta}$  equal to  $-1.0$  and  $-0.1$  in (b), respectively. (c) The partial density of states of  $e_g$  states in NdNiO<sub>3</sub> by the tight binding model. The orbital polarization can be clearly seen.

Fig. 3. The energy bands  $E(\vec{k})$  for spin structure  $P_6$  of NdNiO<sub>3</sub> by the LSDA+U method (a) and those by the tight binding model (b). The results (b) should be folded along chain line and the resulting E- $\vec{k}$  curves correspond to those in (a). The Slater-Koster parameter  $V_{dd\sigma}$  and  $V_{dd\delta}$  equal to  $-1.0$  and  $-0.1$  in (b), respectively. (c) The partial density of states of  $e_g$  states by the tight binding model. The separation of partial density of states does not exist. (d) The contour plot of  $E(\vec{k})$  of the corresponding tight-binding model Hamiltonian. The  $\vec{g}_a$  and  $\vec{g}_b$  are the basis set of the reciprocal lattice, and the corresponding translation vectors are  $\vec{a} = (1, 0, -1)$  and  $\vec{b} = (0, 1, -1)$ . Translation vector  $\vec{c}$  and a corresponding vector  $\vec{g}_c$  are parallel to  $(1, 1, 1)$ .

## References

- [1] J. L. García-Muñoz, J. Rodríguez-Carvajal, P. Lacorre and J. B. Torrance, Neutron-diffraction study of RNiO<sub>3</sub>(R=La,Pr,Nd,Sm): Electronically induced structural changes across the metal insulator transition, Phys. Rev. B **46** (1992), 4414–4425.
- [2] J. A. Alonso, J. L. García-Muñoz, M. T. Fernandez-Díaz, M. A. G. Aranda, M. J. Martínez-Lope and M. T. Casais, Charge disproportionation in rnio<sub>3</sub> perovskites: simultaneous metal-insulator and structural transition in YNiO<sub>3</sub>, Phys. Rev. Lett. **82** (1999), 3871–3874.
- [3] J. L. García-Muñoz, J. Rodríguez-Carvajal and P. Lacorre, Neutron-diffraction study of the magnetic order in the insulating regime of the perovskites RNiO<sub>3</sub> (R=Pr and Nd), Phys. Rev. B **50** (1994), 978–992.
- [4] S.Yamamoto and T.Fujiwara, in preparation.
- [5] J. M. Hastings, L. M. Corliss, W. Kunnmann and S. La Placa, Magnetic structure of calcium vanadate, J. Phys. Chem. Solids **28** (1967) 1089–1092.

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